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Non-Destructive Characterization of Polymer/Metal Interfaces Using Surface-Enhanced Raman Scattering (SERS)

by

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Surface-enhanced Raman scattering (SERS) is an analytical technique in which the Raman scattering cross-sections of molecules adsorbed onto the roughened surfaces of certain metals are enhanced by as much as six orders of magnitude compared to their value for normal Raman scattering. Many models have been proposed to explain SERS, but it is now considered that most of the enhancement is related to two mechanisms. The first is associated with the large electric fields that can be induced at the surfaces of metal particles having small radii of curvature. The second is associated with formation of charge-transfer complexes between the adsorbed molecules and the substrate. Enhancement due to the charge transfer mechanism is obtained only for molecules immediately adjacent to the surface, but enhancement due to electromagnetic mechanism may extend several monolayers away from the surface. Considering that normal Raman scattering by polymers is weak and that scattering by molecules adjacent to the substrate is strongly enhanced, it is

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19. Abstract (continued)

evident that SERS can be used for non-destructive characterization of interfaces between polymer films and metals as long as the films are not so thick that scattering by the bulk of the film is comparable in intensity to SERS from the interface. SERS can be used to obtain a great deal of information about the interface, including the identity and orientation of adsorbed species and mechanisms of adsorption.

We have used SERS to examine the interface between silver and an acrylic adhesive system consisting of an acrylic monomer and a cure system consisting of cumene hydroperoxide (CHP), acetylphenylhydrazine (APH) and saccharin. SERS spectra obtained from films of the adhesive spin-coated onto silver island films were similar to normal Raman spectra of salts of saccharin, indicating that saccharin had adsorbed on the silver dissociatively. The spectra were independent of the thickness of the adhesive films, indicating that the SERS signal was characteristic of the interface and not of the bulk adhesive.

SERS has also been used to characterize the interface between silver and pyromellitic diimide (PMDI), a model compound for polyimides. SERS spectra of PMDI adsorbed onto silver were considerably different from normal Raman spectra. The strongest band in the normal spectra, a carbonyl stretching mode near 1770 cm^{-1}, was absent from the SERS spectra and a band near 700 cm^{-1} which was very weak in normal Raman spectra was strong in SERS spectra. It was inferred that PMDI was adsorbed with a vertical conformation with one imide group adjacent to the surface.

cont.-BLOCK 18- Keywords; Cumene Hydroperoxide (CHP), Acetylphenylhydrazine (APH); Saccharin, Pyromellitic diimide (PMDI)